

DEGRADATION STUDIES ON NICKEL NITRATE HEXAHYDRATE. PART 1. EFFECT OF EXPERIMENTAL CONDITIONS

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(Received 1 October 1984)

ABSTRACT

Previous studies of the effect of heat on nickel nitrate hexahydrate have been reviewed. Many reports are conflicting in their description of observed intermediates. This study has resolved these differences in terms of variations in experimental conditions. The deaquation of nickel nitrate hexahydrate can be seen to be greatly influenced by factors such as sample size, heating rate and atmosphere.

INTRODUCTION

During the past two decades inorganic salts have assumed increasing importance in a wide variety of applications. They are useful as reaction media, in metallurgical processes, in electrochemical power sources, as precursors in the preparative chemical industry, and as heterogeneous and homogeneous catalysts. In most of these uses the knowledge of degradation processes and thermal interactions of such salts is of great value. Stern [1] remarks that attention in this field has been focused mainly on the alkali and alkaline earth halides. Even if one disagrees with Stern it is true that in many other cases the thermal interactions and processes are not well defined and in certain cases not even the range of thermal stability is known.

A detailed knowledge of the mechanisms by which compounds degrade can give an insight into the behaviour and basic chemistry of many species. Thus studies of simple salts of a transition metal can give indications as to

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the behaviour of that metal in complexes having a biological significance. The aim of this study was to look critically at the decomposition of nickel nitrate. The work described here focuses on the effects of heating rate, atmosphere and sample size in an attempt to understand better the often conflicting reports already published. Subsequent parts of the study [2,3] will describe mechanistic studies using infrared and Raman spectroscopy. Supplementary results have also been obtained for nickel nitrate hexammine and an anhydrous nickel nitrate salt.

PREVIOUS WORK

Mellor [4] has reviewed the thermochemistry of nickel nitrate up to 1936. He noted that the hexahydrate undergoes a transition to the trihydrate at approximately 328 K and a basic nitrate and nickel peroxide can be formed. The anhydrous salt, prepared from the action of nitrogen pentoxide on the hydrated salts, was a pale greenish-yellow powder which began to decompose at 378–383 K evolving nitrous fumes. It has also been noted that the loss of nitric acid occurred when the dehydration was carried beyond the loss of four molecules of water forming a salt of orthonitric acid, this being [5] a hypothetical compound $\text{O}=\text{N}-(\text{OH})_3$. The melting point of the hexahydrate has been determined as 329.7 K.

Wendlandt [6] studied the thermal decomposition of a series of metal nitrates using thermogravimetry (TG) with a heating rate of 5.4 K min^{-1} in a slow stream of air. He found that nickel nitrate hexahydrate began to lose water at 323 K. After a period of rapid mass loss, a break in the curve was observed at 478 K which he reported as corresponding to the formation of the anhydrous salt. Further rapid mass loss took place above 478 K resulting in the NiO level at 778 K.

Jaffray and Rodier [7] studied the crystalline transitions of nickel nitrate hexahydrate between 113 and 273 K using differential thermal analysis (DTA) and dilatometry. They found that it undergoes three crystalline transitions at 150, 169 and 205.5 K and two polymorphic transformations at 238 and 259 K.

Later Duval [8], in a treatise on inorganic thermogravimetry reported that when nickel nitrate hexahydrate was heated rapidly ($100\text{--}180 \text{ K h}^{-1}$) it melted at 330 K yielding a dark green liquid. At 553 K a yellow and green solid was obtained; this gradually became black, forming pure nickel oxide at 613 K. When heated slowly (5–10 K per day) the green tetrahydrate appeared at 323 K, the pale green dihydrate at 363 K, a greyish-green solid mixture at 453 K, and pure nickel oxide at 513 K.

Wheeler and Frost [9] reported on the rate of dehydration at several vapour pressures of water. They found evidence for the existence of a tetrahydrate intermediate, the end product being the dihydrate. The highest

temperature used was 333 K and the possibility of the formation of a basic salt was disregarded since it was found that all products reverted to the hexahydrate after standing in the room atmosphere for a few hours. Van My [10] studied the dehydration using a microcalorimeter with heating rates of approximately 10 K h^{-1} . The results are essentially equivalent to those obtained by differential scanning calorimetry (DSC). He has calculated the heats of reaction for each peak observed.

Weigal et al. [11,12] studied the decomposition of nickel nitrate hexahydrate at a variety of heating rates using a calorimeter and found, depending on the conditions used, evidence for the following species:

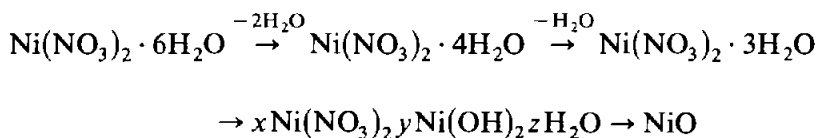
nickel nitrate hexahydrate (reactant)	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
nickel nitrate tetrahydrate	$\text{Ni}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$
nickel nitrate dihydrate	$\text{Ni}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$
nickel nitrate (anhydrous)	$\text{Ni}(\text{NO}_3)_2$
basic nickel nitrate	$\text{Ni}(\text{NO}_3)_2 \cdot 2\text{Ni}(\text{OH})_2$
nickel oxide (product)	NiO

However Lumme and Peltonen [13] in a TG study of the nickel salt using a heating rate of 5.5 K min^{-1} found no detectable intermediate hydrates. They noted that dehydration began at 303 K and that a break in the curve appeared at 555 K corresponding to $\text{Ni}(\text{NO}_3)_{1.33}(\text{OH})_{0.67}$.

Keely and Maynor [14] conducted thermal studies on nickel, cobalt, iron and copper nitrates and oxides. All their experiments were conducted in flowing air with a heating rate of $\sim 5 \text{ K min}^{-1}$. They found that nickel nitrate hexahydrate lost slightly more than one mole of water at 473 K. A temperature of approximately 673 K was needed before complete decomposition to nickel oxide occurred. The mass loss was moderately uniform and the red-brown fumes of nitrogen dioxide appeared before 523 K had been reached. They infer from this that compound decomposition occurs before four moles of water are lost. They note that a lower heating rate (unspecified) resulted in the decomposition starting at lower temperatures. Their TG trace indicates the existence of a stable nickel compound at 483 K; the mass loss corresponding to a nickel basic nitrate compound containing approximately 1.5 molecules of H_2O . They think it unlikely that anhydrous nickel nitrate was ever present, this contrasting with the conclusion of Wendlandt [6] using similar conditions.

Prost and Robin [15] found that under vacuum (10^{-2} Torr) two stages of the dehydration of the dihydrate could be observed under isothermal conditions, the first having an activation energy of 99.5 kJ mol^{-1} and the second $122.6 \text{ kJ mol}^{-1}$. The first stage was found to have a reaction order of $2/3$ whilst the second had an order of approximately 1.6. Kalinichenko and Purtov [16] studied the decomposition in a water vapour-air medium using TG, DTA and EGA, the latter measuring the liberation of the oxides of nitrogen calculated as NO. They found an endothermic effect at 328 K, this being unassociated with any mass loss. A further small effect at 383 K was

accompanied by the loss of about 0.2 molecules of water. They detected the start of the decomposition of the nickel nitrate at 400 K by chemical analysis of the reactant at this stage. However, this was insignificant until a temperature of 447 K was reached when the EGA system detected NO. The decomposition was found to be stepwise, thus



where x and z are unspecified constants and y was found to be approximately 1.16. In a further paper Kalinichenko and Purtov [17] discussed the possibility of differing oxides of nickel being produced by various conditions of decomposition. However, by heating the hexahydrate isothermally for different times and for different thicknesses of layer they found only NiO in each case.

Auffredic et al. [18], acknowledging previously published work showing the existence of stoichiometric intermediates during the dehydration of nickel nitrate, measured the enthalpy of dehydration from the hexa- to the tetrahydrate and found it to be $110.2 \text{ kJ mol}^{-1}$.

Wendlandt [19] studied a series of hydrated nickel salts by DTA using both open and sealed sample tubes. The first group of peaks were identical for all the samples and began at 323 K, ending at 353 K. These corresponded to the hexa- to tetrahydrate transition, ending in the samples undergoing a phase transition from solid to liquid. The DTA trace for nickel nitrate hexahydrate using an open sample tube showed a number of small peaks in the temperature range 398–448 K which Wendlandt ascribed to the decomposition of the lower hydrates.

Dollimore and Pearce [20] used surface area measurements to complement their TG studies of a series of nickel salts including the nitrate. The products, after different times of heating at 4 K min^{-1} in flowing, dry CO_2 , were cooled and their surface areas determined. They found that, unlike other nickel salts, the dehydration of nickel nitrate hexahydrate was not accompanied by an overall increase in surface area. However, since the salt melts initially, as discussed earlier, the cooling process would only have produced crystalline products of similar surface areas, as opposed to products containing shattered crystalline forms produced if no melting had occurred.

It can be seen from the preceding survey that there seems to be general agreement that a number of stoichiometric nickel nitrates are formed as intermediates when the hexahydrate is heated. However not all workers have reported the formation of an anhydrous nitrate and many have found forms of basic nickel nitrates.

EXPERIMENTAL

Thermogravimetry was achieved using a vacuum microbalance system. This consisted of a CI Electronics balance linked to a vacuum manifold capable of being pumped down to 10^{-6} Torr. A small glass crucible was used to hold the sample. This was sufficiently open so as to avoid the effects of back pressure from the evolved gases. A number of expansion bulbs were connected to the manifold enabling decompositions to be performed in static atmospheres of known composition and pressure. Heating was by a furnace controlled by a Stanton-Redcroft linear temperature programmer (Mk. 3). Temperature measurement was via a thermocouple placed 1 mm below the crucible.

DTA was achieved using a Stanton-Redcroft 671 unit. Vacuum was obtained by a two-stage rotary pump. Throughout the work there was never any evidence of the furnace design, with its small swept volume and narrow gas exit path, giving rise to any spurious results.

The nickel nitrate hexahydrate used was AnalaR grade material. The sample was a single crystal of approximate mass 10 mg unless otherwise stated.

RESULTS

TG data are presented here in the form of the fraction decomposed, α , with temperature, T . Thus the α - T trace derived from the TG unit for the vacuum (10^{-6} Torr) decomposition of nickel nitrate hexahydrate is shown in Fig. 1. As can be seen the processes of dehydration and decomposition are complex and multistaged. The final mass loss was 73.83%, corresponding well with the theoretical mass loss of 74.23% for a final product of NiO. The different stages of the overall dehydration process correspond well with the formation of five integral and half integral hydrate intermediates, viz. species containing 5.5, 4.5, 3, 2.5 and 2 molecules of water and in addition a compound corresponding to anhydrous nickel nitrate.

Figure 2 shows the α - T trace for the decomposition of the material in the presence of 2 Torr water vapour pressure. As can be seen the trace is very different to that for the vacuum decomposition up to 400 K after which the two traces are almost identical. Up to this point the dehydration is more rapid, the dihydrate being reached at 350 K, approximately 55 K lower than before. This points to the operation of a Smith-Topley [21] effect whereby the rate of dehydration or dehydroxylation rises to a maximum with increasing water vapour pressure.

Figure 3 shows the α - T traces for the decomposition of a range of sizes of single-crystal nickel nitrate hexahydrate. As can be seen, the traces differ up to a temperature of 400 K, the mass at this point corresponding to the

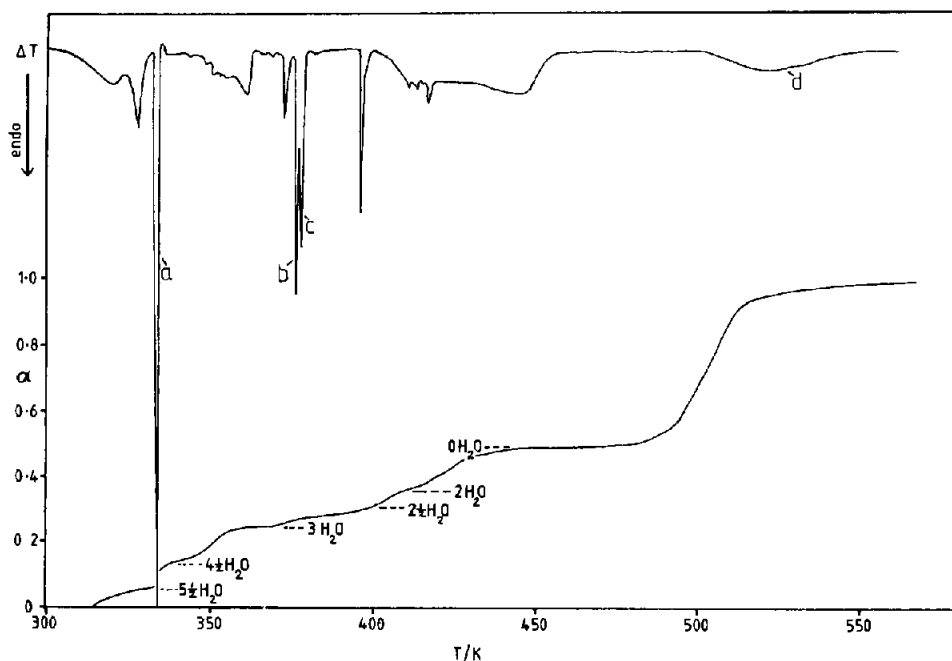


Fig. 1. Plot of α versus T for the vacuum decomposition of nickel nitrate hexahydrate at 1 K min^{-1} by TG together with the DTA trace for the same process.

dihydrate. Prior to this point there are several variations in the number of hydrates observed and in the temperatures of dehydration. In general there are three factors involved in the decomposition of different sized crystals.

(1) Since the ratio of surface area to volume for small crystals is greater than that for large crystals, the rate of loss of gaseous products will be greater. Thus diffusion-controlled processes should be faster for smaller crystals.

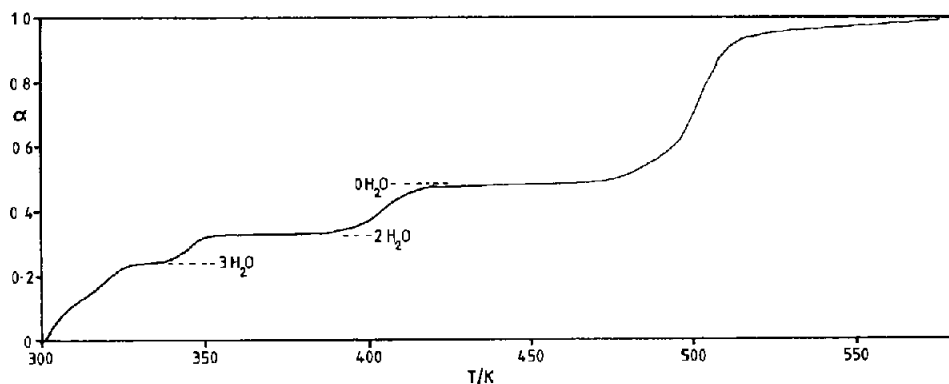


Fig. 2. Plot of α versus T for the decomposition of nickel nitrate hexahydrate at 1 K min^{-1} by TG in the presence of 2 Torr water vapour.

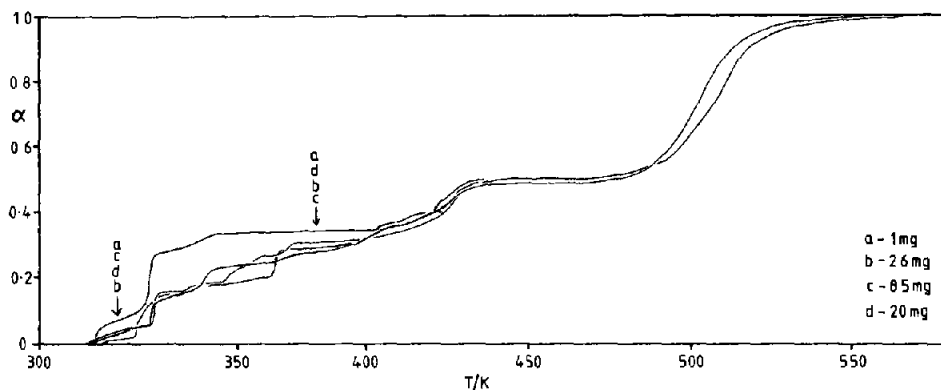


Fig. 3. Plot of α versus T for the vacuum decomposition of a range of sizes of single crystal nickel nitrate hexahydrate at 1 K min^{-1} by TG.

(2) There will always be a better vacuum around a smaller crystal. If the heat transfer to the sample is predominantly via convection, as will be the case at low temperatures, then smaller crystals may be at a lower temperature than larger ones.

(3) There is less of a temperature gradient through a smaller crystal, leading to greater precision in α - T traces. Also endo- or exothermic effects are minimized with smaller sample sizes.

The first point, involving a more rapid removal of product gases from a smaller crystal may in fact reduce the overall rate of decomposition. In a large crystal the prolonged evolution of, say, water vapour during a dehydration may affect the next stage of dehydration if a Smith-Topley effect is in operation [22]. However if some of the stages of dehydration are controlled by equilibrium processes then the opposite result, i.e., a speeding up of dehydration processes with higher vacuum conditions, would apply. All these points may account for the lack of any observable trends in the traces for the 1.0, 2.6, 8.5 and 20 mg samples. The smallest sample is clearly the most different, forming the dihydrate at 354 K. The traces for each sample mass show plateaus for different hydrates up to the formation of the dihydrate. Considering the starting material to have the formula $\text{Ni}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$ where $n = 6$, then the values of n corresponding to intermediate hydrates observed during these experiments are 5.5, 4.5, 4, 3.5, 3, 2.5 and 2.

The α - T trace for the vacuum decomposition of nickel nitrate hexahydrate using a heating rate of 5 K min^{-1} is shown in Fig. 4. As is to be expected the stages of dehydration are not as clearly defined as those obtained using a lower heating rate. Together with the main decomposition they occur at higher temperatures than previously although the temperature at which $\alpha = 1.0$ is reached is only marginally higher at 610 K. Figure 5 shows the α - T trace for the decomposition of the hexahydrate in static air using a heating rate of 1 K min^{-1} . Once again the initial part of the trace shows the

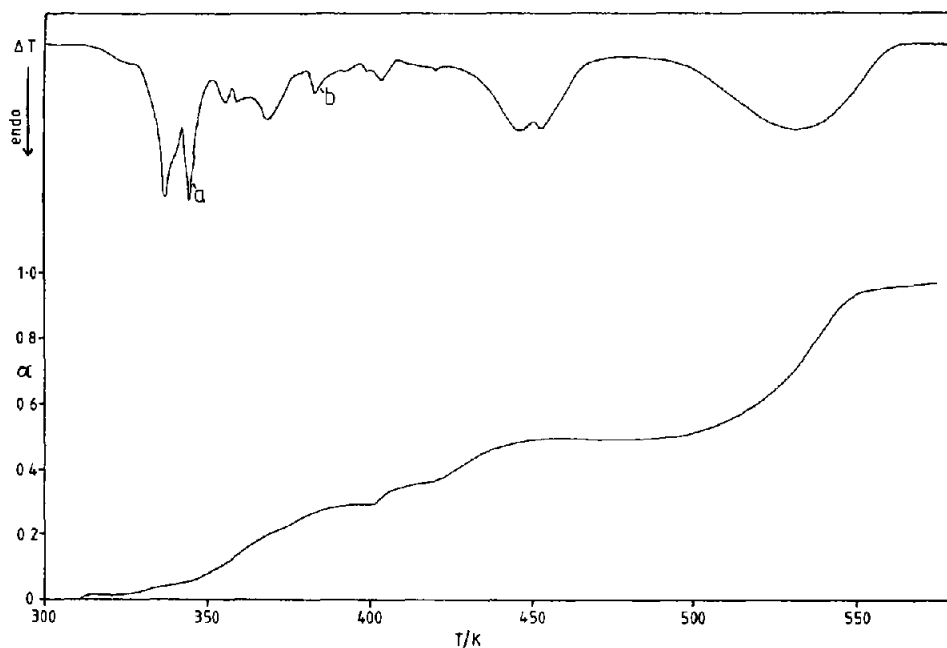


Fig. 4. Plot of α versus T for the vacuum decomposition of nickel nitrate hexahydrate at 5 K min^{-1} by TG together with the DTA trace for the same process.

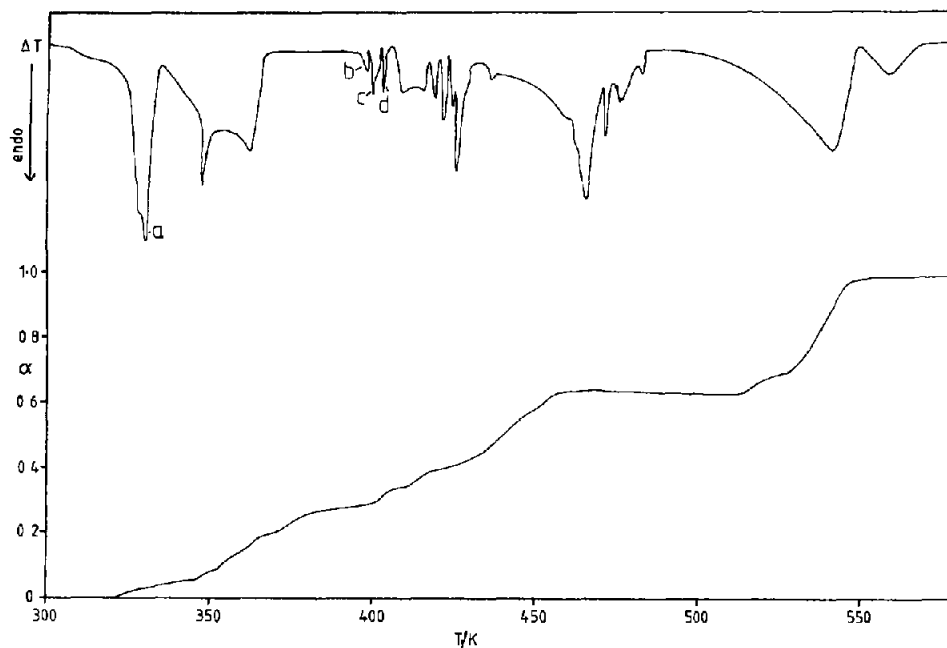


Fig. 5. Plot of α versus T for the decomposition of nickel nitrate hexahydrate at 1 K min^{-1} in static air by TG together with DTA trace for the same process.

formation of a number of hydrates. However, unlike the other traces described so far, the initial mass loss continues past the $\alpha = 0.50$ stage until at a temperature of 457 K a plateau at $\alpha = 0.66$ is reached. This remains constant until approximately 510 K when the main decomposition begins. However, again this is different; an inflection occurs at $\alpha = 0.69$ dividing the final stage into two sections. The plateau at $\alpha = 0.66$ corresponds to a compound of formula $2\text{Ni}(\text{NO}_3)_2\text{Ni}(\text{OH})_2$ (theoretical $\alpha = 0.639$) or $\text{Ni}(\text{NO}_2)_2$ (theoretical $\alpha = 0.648$). If the curve prior to the inflection at $\alpha = 0.69$ is extrapolated then a plateau at $\alpha = 0.70$ is produced. This corresponds with a compound of formula $\text{Ni}(\text{NO}_3)_2$ (theoretical $\alpha = 0.708$). This suggests that the earlier compound is also a basic nitrate and not the nitrite. Figure 6 shows the decomposition of nickel nitrate hexahydrate in static air with a heating rate of 5 K min^{-1} . In common with the trace for vacuum decomposition using the same heating rate, the stages of dehydration are not clearly defined. However the distinguishing inflections on the trace occur at higher temperatures and pure NiO is only formed at approximately 630 K. The final main decomposition curve is preceded by an inflection which if extrapolated produces a plateau at $\alpha = 0.60$. This corresponds well with the basic nitrate $3\text{Ni}(\text{NO}_3)_2\text{Ni}(\text{OH})_2$ (theoretical $\alpha = 0.604$).

The DTA trace for the vacuum decomposition of nickel nitrate hexahydrate using a heating rate of 1 K min^{-1} is shown in Fig. 1. From direct visual

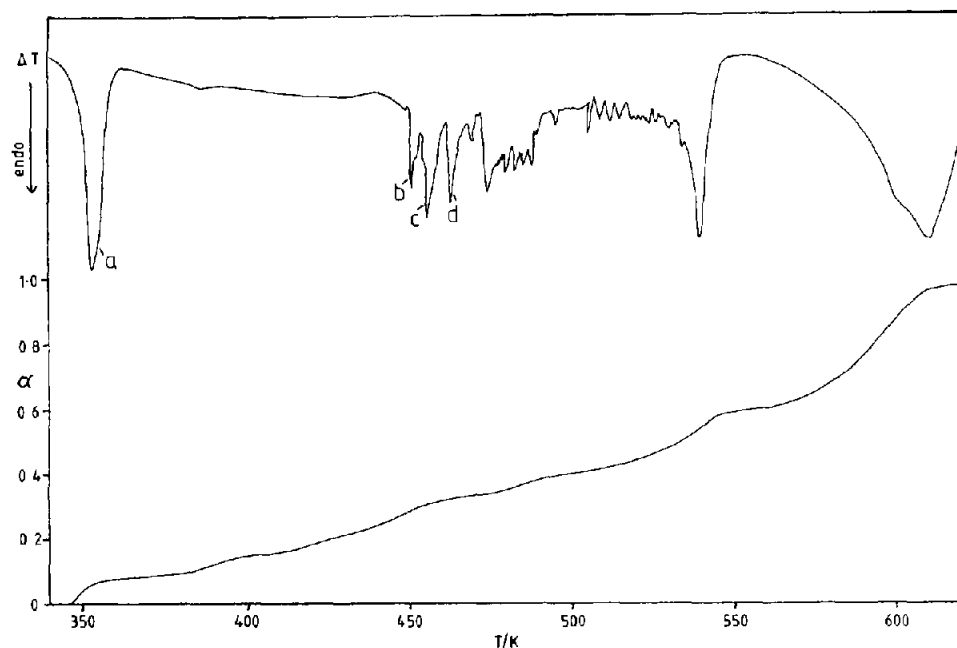


Fig. 6. Plot of α versus T for the decomposition of nickel nitrate hexahydrate at 5 K min^{-1} in static air by TG together with the DTA trace for the same process.

observation through the viewing port in the DTA instrument, peak a corresponds to complete liquefaction of the sample and peaks b and c to the solidification of the sample. The sample remained green in colour up to a temperature of approximately 450 K and gradually blackened until approximately 495 K. This last temperature corresponds with the beginning of the last peak, associated with the main decomposition. It may be that the gradual blackening observed is only due to surface decomposition, bulk decomposition giving peak d. Figure 4 shows the DTA trace for the vacuum decomposition of the salt using a heating rate of 5 K min^{-1} . Peak a corresponds to complete liquefaction of the sample and peak b to the subsequent solidification.

Figure 5 shows the DTA trace for the decomposition of the material in static air using a heating rate of 1 K min^{-1} . Peak a corresponds to the liquefaction of the sample and peaks b, c and d to the solidification. The portion of the trace from 473 to 485 K was marked by a degree of oscillation in the signal obtained from the sample. Unlike the results obtained in vacuum this trace contains two peaks corresponding to the final conversion of the sample to the black nickel oxide. The DTA trace for the decomposition of the salt in static air using a heating rate of 5 K min^{-1} is shown in Fig. 6. Peak a and peaks b, c and d correspond to the liquefaction and subsequent solidification of the sample, respectively. A large amount of apparent noise in the trace was observed between 472 and 534 K. The final conversion of the sample to nickel oxide is characterized by two overlapping peaks, although as observed in all the previous experiments the sample appeared to be black shortly after the onset of the main peak(s).

In general, comparing the DTA results obtained using heating rates of 1 K min^{-1} with those at 5 K min^{-1} , it can be seen that the peaks using the lower heating rate are fairly sharp and small. In contrast, those obtained using the larger heating rate are larger and broader. This is to be expected providing that the sample sizes are the same throughout [23]. In all cases solidification of the sample resulted in a number of peaks or double peaks. This was attributed to the presence of a number of small globules of molten sample present in the crucible prior to solidification. These were caused by the, often violent, evolution of product gases during the decomposition.

DISCUSSION

The thermal analysis studies of nickel nitrate hexahydrate are best considered in terms of three overall processes or sections which appear to be present. The first of these involves the loss of water ending in the formation of the dihydrate. The second section involves further mass loss ending with the formation of a stable solid intermediate. The third section is the decomposition of the latter intermediate, ending with the formation of the product, nickel oxide.

Considering the first section it is evident that every integral and half integral hydrate possible between the hexa- and dihydrate has been observed in one or more of the TG experiments. Previous work has only resulted in the formation of three of these, namely the tetra-, tri- and dihydrates and none of the studies found all three in any one experiment. This indicates that the main conditions used here, namely a low heating rate and vacuum, are conducive to the early removal of potential gaseous products with the formation of stable, solid intermediates.

In order to understand the appearance of the integral and half integral hydrates it is necessary to describe briefly the coordination chemistry of divalent nickel. For any nickel compound containing a number of potential ligands the formation of a six-coordinate species is favoured [24]. However, here the number of available ligands is being continuously reduced. Bjerrum [25] noted that nickel is unusual in that there is no single coordination number below that of six of any special significance and that no one will be favoured.

The four-coordinate, planar complexes of divalent nickel are usually red, yellow or brown whereas the six-coordinate octahedral complexes are green (for oxygen-containing ligands) or blue/purple (for ammine-type ligands) as are the tetrahedral complexes although in the latter case there are exceptions [24]. Five-coordinate complexes of divalent nickel have various colours, depending on the ligands. Visual observations during the DTA experiments showed that the nickel dehydration products were always shades of green. This indicates that the nickel was, in general, able to maintain an octahedral field. This would undoubtedly be helped by the ability of water to act both as a unidentate ligand and as a bridging ligand which explains the appearance of half integral hydrates.

The influence of water vapour on the dehydration processes, as described earlier, is by no means unusual. Brown et al. [26] discuss the appearance of this type of behaviour for a series of crystalline hydrates. It is interesting that it is the dihydrate which is reached rapidly during decomposition in the presence of water vapour. In view of the foregoing discussion this suggests that there are no more potential ligands readily available in the compound at this point.

Turning to the TG and DTA traces for nickel nitrate hexahydrate decompositions in vacuum at 5 K min^{-1} and static air at 1 and 5 K min^{-1} , further points can be made. The TG trace for the decomposition at 5 K min^{-1} in vacuum is, as described earlier more uniform than for a heating rate of 1 K min^{-1} . At higher heating rates TG curves are more likely to be smooth if the processes are diffusion controlled. However, the 2.5 and 2 hydrate intermediates are clearly formed and so the transition between these two may have a different rate-controlling step. It is interesting that the DTA trace is also much smoother, with less pronounced peaks. This may be because the liquid state has become more of a solution and less of a melt than before

thus enabling changes to occur more readily. The reason for the absence of the large peak during the 2.5 to 2 hydrate stage is unclear but it may be because the 2.5 hydrate is already of a similar structure, i.e., octahedral, to the 2 hydrate.

Comparison of the TG and DTA traces for the decomposition in air at 1 K min^{-1} reveals that there are no DTA peaks during the transformation between the 3.5 and 2.5 hydrates. Both of these compounds are clearly dimeric in nature but a structural rearrangement would be necessary during the transition. However the TG does not show the 3.5 hydrate as being a clear intermediate and it may be that the 2.5 hydrate is formed at that point, leaving the water to slowly diffuse out of the sample. Indeed the sample does not solidify until the 2.5 hydrate is reached and so the sample may be a solution. The decomposition in air at 5 K min^{-1} shows similar behaviour over a wider range. In this case there are no DTA peaks between the 5.5 and 2.5 hydrates.

Thus the first section of the decomposition of nickel nitrate hexahydrate, from the hexahydrate to the dihydrate is probably governed by two overall processes. In vacuum the main consideration appears to be the availability of potential ligands to enable an octahedral structure to be maintained. In air, however, this is moderated by the difficulty in removing water from the sample. This leads to a situation where saturated solutions may be formed. Within these ligands availability may still be a prime consideration but, as regards the observable mass loss this is a reflection of the ease of evaporation of water from the sample.

Turning to the second stage of the decompositions, it is clear from the dihydrate to the last intermediate that there are fundamental differences between the experiments conducted under different conditions. Under vacuum the next intermediate formed after the dihydrate corresponded to $\text{Ni}(\text{NO}_3)_2$. However in static air the basic nitrates $n\text{Ni}(\text{NO}_3)_2\text{Ni}(\text{OH})_2$ ($n = 1, 2$ and 3) were observed. This indicates that the nitrate can be hydrolysed by water vapour. This in turn explains why some workers have observed basic nickel nitrates and others have not. In addition, as described earlier, it has been reported that HNO_3 is evolved from samples prior to complete loss of water. If this has not arisen from reactions between NO_2 and water vapour around the sample then it may be that hydrolysis involving water present within the nitrate may occur. This may happen if temperatures at which hydrolysis reactions are favoured are reached prior to complete water loss.

The TG trace for the decomposition in static air at 1 K min^{-1} shows the formation of two basic nitrate compounds. These, together with the number reported in the literature described earlier, indicate that a large number of such stoichiometric compounds can be formed depending on the conditions used. The portion of the DTA trace from the 2.5 hydrate to the $2\text{Ni}(\text{NO}_3)_2 \cdot \text{Ni}(\text{OH})_2$ intermediate does not match the TG trace very well (Fig. 5). This is

probably due to the volume of the space around the sample being very small in the DTA instrument, this providing a dampening effect on reactions involving atmospheric gases.

It is interesting to note that the presence of 2 Torr water vapour during the decomposition of the hexahydrate did not lead to the formation of a basic nickel nitrate compound. This would suggest that the hydrolysis process only occurs above a certain pressure of water vapour.

The ease of hydrolysis of the nickel nitrate is probably a reflection of the instability of the nitrate species at these temperatures. Certainly the OH species are no more versatile as ligands than are the nitrate species. However they are smaller ligands and much stronger. Thus each successive decrease in n for $n\text{Ni}(\text{NO}_3)_2 \cdot \text{Ni}(\text{OH})_2$ may lead to a more compact and stable structure thus making further hydrolysis harder. This may be what is being seen during the decomposition in static air at 1 K min^{-1} where a higher temperature is needed to go from $n = 2$ to $n = 1$. Clearly a temperature is reached where the entire structure becomes unstable and so bulk decomposition occurs.

SUMMARY

The deaquation of nickel nitrate hexahydrate is thus a process dominated by three factors. The first is the coordination chemistry of nickel and the subsequent importance of ligand availability. Different stages of the deaquation reactions can be viewed as continual demonstrations of the preferred six-coordinate nature of divalent nickel. The second is the ease of removal of water from the sample, this being predominantly a diffusion-controlled process. The third factor is the reactivity of water vapour and its ability to hydrolyse nickel nitrate dihydrate.

REFERENCES

- 1 K.H. Stern, *J. Phys. Chem. Ref. Data*, 1 (1972) 247.
- 2 D. Dollimore, G.A. Gamlen and T.J. Taylor, to be published.
- 3 D. Dollimore, G.A. Gamlen, T.J. Taylor, A.J. Barnes and M.A. Stuckey, to be published.
- 4 J.W. Mellor, *Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Longmans, London, 1936, Vol. 16, p. 487.
- 5 J. Grant (Ed.), *Hackh's Chemical Dictionary*, McGraw-Hill, New York, 1969, p. 478.
- 6 W.W. Wendlandt, *Texas J. Sci.*, 10 (1958) 392.
- 7 J. Jaffray and N. Rodier, *C.R. Acad. Sci.*, 238 (1954) 1975.
- 8 C. Duval, *Inorganic Thermogravimetric Analysis*, 2nd edn., Elsevier, Amsterdam, 1963, p. 360.
- 9 R.C. Wheeler and G.B. Frost, *Can. J. Chem.*, 33 (1955) 56.
- 10 M. Le Van My, *Bull. Soc. Chim. Fr.*, (1964) 545.
- 11 D. Weigal, B. Imelik and P. Laffitte, *Bull. Soc. Chim. Fr.*, (1962) 345.

- 12 D. Weigal, B. Imelik and M. Prettre, *C.R. Acad. Sci.*, 14 (1964) 2215.
- 13 P. Lumme and J. Peltonen, *Suom. Kemistil.*, 37 (1964) 162.
- 14 W.M. Keely and H.W. Maynor, *J. Chem. Eng. Data*, 8 (1963) 297.
- 15 M. Prost and J. Robin, *C.R. Acad. Sci.*, 257 (1963) 1097.
- 16 I.I. Kalinichenko and A.I. Purtov, *Russ. J. Inorg. Chem.*, 11 (1966) 891.
- 17 I.I. Kalinichenko and A.I. Purtov, *Russ. J. Inorg. Chem.*, 11 (1966) 1186.
- 18 J.P. Auffredic, C. Carel and D. Weigal, *C.R. Acad. Sci.*, 275 (1972) 5.
- 19 W.W. Wendlandt, *Thermochim. Acta*, 9 (1974) 101.
- 20 D. Dollimore and J. Pearce, *J. Therm. Anal.*, 6 (1974) 321.
- 21 B. Topley and M.C. Smith, *J. Chem. Soc.*, (1935) 321.
- 22 H.W. Quinn, R.W. Missen and G.B. Frost, *Can. J. Chem.*, 33 (1955) 286.
- 23 R.C. Mackenzie and B.D. Mitchell, in R.C. Mackenzie (Ed.), *Differential Thermal Analysis*, Academic Press, New York, 1970, p. 101.
- 24 F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 3rd edn., Interscience, New York, 1972, p. 528.
- 25 J. Bjerrum (Ed.), *Metal Ammine Formation in Aqueous Solution*, Haase, Copenhagen, 1957.
- 26 W.E. Brown, D. Dollimore and A.K. Galwey, in C.H. Bamford and C.H.F. Tipper (Eds.), *Comprehensive Chemical Kinetics*, Vol. 22, *Reactions in the Solid State*, Elsevier, Amsterdam, 1980.